An Experimental and Theoretical Study of the Basicity of Tetra-*tert*-butyltetrahedrane

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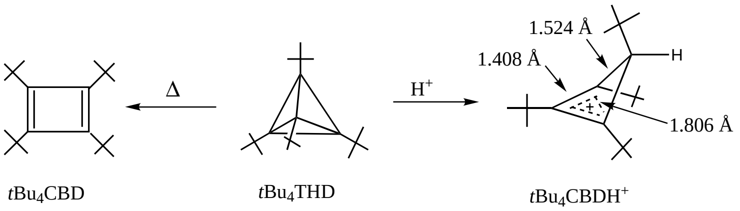
Abstract: The gas-phase basicity (GB) of tetra-*tert*-butyltetrahedrane (tBu$_4$THD) was determined by FT-ICR mass spectrometry and comparison with reference compounds of known basicity. Its GB, 1035 ± 10 kJ mol^{-1}, makes tetra-*tert*-butyltetrahedrane one of the strongest bases reported so far. Ab initio calculations [B3LYP/6-31G(d) and B3LYP/6-311 + G(d,p)//6-31G(d)] have been carried out in order to compare the high experimental basicity of tBu$_4$THD with that estimated theoretically. Both B3LYP/6-31G(d) and QCISD(T) calculations were used to determine the reaction path which connects the initial tetrahedrane–ammonium complex with the final products, protonated cyclobutadiene (CBDH$^+$) and ammonia.

Keywords: ab initio calculations · basicity · cyclobutadienes · strained molecules · superbases · tetrahedranes

Introduction

The problem of synthesizing tetrahedrane (THD, see ref. [1] for the abbreviations used throughout this study) was recognized more than half a century ago. It stimulated an intensive search to find a method of preparation from suitable precursors,[2] and eventually resulted in the isolation and complete structural characterization of tetra-*tert*-butyltetrahedrane (tBu$_4$THD).[3–5] Although the energy required to break the C$-$C bond of THD is a mere 42 kJ mol^{-1} (DZ + P basis set with electron correlation),[7] as a result of the enormous angular strain ($E_{\mathrm{str}} = 585$ kJ mol^{-1}, HF/6-31G*),[6] numerous ab initio and semiempirical calculations[2d, 8] consistently indicate high kinetic stability of tetrahedrane in the absence of other reactants. In tBu$_4$THD and in other recently prepared, very stable derivatives of tetrahedrane,[9–15] the above-mentioned lability is circumvented by means of spatial shielding of the tetrahedrane framework by four bulky groups, the so-called "corset effect".[2d, 15]

Although high-level theoretical calculations (G2) predicted THD to be a superbase[16] with a proton affinity (PA) at 298 K of 1053 kJ mol^{-1} (as well as a very strong carbon acid),[17] no experimental data on the basicity of tetrahedranes existed. Two properties of tBu$_4$THD relevant for this study have to be kept in mind: firstly, tBu$_4$THD is higher in energy than tetra-*tert*-butylcyclobutadiene (tBu$_4$CBD). NMR experiments allows one to conclude that the amount of tBu$_4$THD in the thermal equilibrium with tBu$_4$CBD is < 1 %; therefore, ΔG^0 should be > 10 kJ mol^{-1}.[5] The transformation of the tetrahedrane into the cyclobutadiene has an activation barrier of $\Delta H^{\neq} = 107 \pm 10$ kJ mol^{-1}.[5] Secondly, tBu$_4$THD forms the homocyclopropenylium ion tBu$_4$CBDH$^+$ upon treatment with gaseous HCl. The structure of tBu$_4$CBDH$^+$ has been determined (Scheme 1).[2d, 18] This paper will report the experimental evidence of the tremendous basicity of this compound and theoretical calculations that will explain the origin of the observed results.



Scheme 1. Reactions of tBu$_4$THD.

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Results and Discussion

Experimental results: The gas-phase basicity, GB, of a base B is formally defined as the standard Gibbs free energy change according to the reaction given in Equation (1), the corresponding proton affinity, PA, being the standard enthalpy change for the same reaction.

$$BH^+(g) \longrightarrow B(g) + H^+(g) \qquad \Delta G^\circ = GB;\ \Delta H^\circ = PA \tag{1}$$

The FT-ICR experiments provide the standard Gibbs free energy changes, ΔGB, pertaining to the proton exchange reaction between B and a reference base, B_{ref} [Eq. (2)]. For this equilibrium, Equation (3) is valid.

$$B(g) + B_{ref}H^+(g) \rightleftharpoons BH^+(g) + B_{ref}(g) \qquad \Delta G^\circ = \Delta GB \tag{2}$$

$$\Delta GB = GB(B_{ref}) - GB(B) = -RT\ln K_p \tag{3}$$

The FT-ICR experiments do no lead directly to proton affinities. The determination of PA therefore requires an independent estimation of the entropy change of the reaction given in Equation (1).

Several strong reference bases were used.[19] With *N,N,N′,N′*-tetramethylguanidine (GB = 997.4 kJ mol^{-1}) and weaker bases, *t*Bu$_4$THD behaves as a stronger base and no equilibrium was reached. In all cases, the peak in the mass spectra corresponding to protonated *t*Bu$_4$THD (*m*/*z* 277) was the predominant one, and the peak of the corresponding protonated reference bases disappeared with time, slowly (at ≈60 s) in the case of *N,N,N′,N′*-tetramethylguanidine. These results indicate that *t*Bu$_4$THD is a very strong base in the gas phase.

To obtain an estimation of the GB of *t*Bu$_4$THD, we used one of the strongest bases commercially available, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, whose basicity was measured by Gal et al.[20] who found a GB value of 1030.2 kJ mol^{-1}.[19]

There is a slow proton transfer from the protonated reference base to *t*Bu$_4$THD; equilibrium is reached within ≈15–60 s. An average K_p value of 5.8 was obtained, and from this a ΔGB between the reference and *t*Bu$_4$THD of 5.0 kJ mol^{-1} resulted, with *t*Bu$_4$THD being a stronger base than 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene. The gas-phase basicity of *t*Bu$_4$THD should be 1035 ± 10 kJ mol^{-1}. This GB value establishes *t*Bu$_4$THD as a superbase in the gas phase.

Computational results and thermodynamic aspects: As we discussed in our theoretical paper,[16] protonation of THD does not yield THDH$^+$ (which we have now verified to have no minimum in the potential energy surface) but CBDH$^+$ instead. Likewise, protonation of *t*Bu$_4$THD leads to the *t*Bu$_4$CBDH$^+$ cation (*m*/*z* 277). All the calculated stationary minima are reported in Table 1 and the corresponding energy profile for the parent system is given in Figure 1.

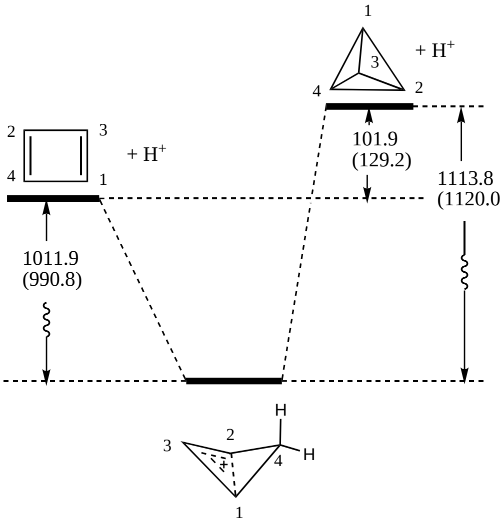

Figure 1. Energy profile for the parent compounds from B3LYP/6-31G(d) and QCISD(T) calculations (in parentheses). All values are given in kJ mol^{-1}.

Note that in Table 1 the comparison of THD and *t*Bu$_4$THD quantifies the thermodynamic part of the "corset effect".[2d, 15] Among the parent compounds, CBD is 101.9 kJ mol^{-1} more stable that THD, while the situation seems to be reversed for the tetra-*tert*-butyl derivative: *t*Bu$_4$THD is calculated to be

Table 1. Absolute energies [Hartree; 1 Hartree = 2625.50 kJ mol^{-1}] and relative energies [kJ mol^{-1}] of the molecules discussed in the text.[a]

Absolute energies	B3LYP/6-31G(d)	B3LYP/6-311 + G(d,p)//6-31G(d)	QCISD(T)/6-31G(d)//B3LYP/6-31G(d)
THD	– 154.636663	– 154.681029	– 154.156754
CBD	– 154.675462	– 154.721129	– 154.205969
CBDH$^+$	– 155.060871	– 155.095893	– 154.583324
*t*Bu$_4$THD	– 783.683294	– 783.887075	
*t*Bu$_4$CBD	– 783.680716	– 783.887546	
*t*Bu$_4$CBDH$^+$	– 784.141692	– 784.340987	
NH$_3$	– 56.547948		– 56.372146
NH$_4^+$	– 56.893889		– 56.719669
Relative energies			
E(THD) – E(CBD)	101.9	105.3	129.2
E(THD) – E(CBDH$^+$)	1113.8	1089.2	1120.0
E(CBD) – E(CBDH$^+$)	1011.9	983.2	990.8
E(*t*Bu$_4$THD) – E(*t*Bu$_4$CBD)	– 6.8	1.2	
E(*t*Bu$_4$THD) – E(*t*Bu$_4$CBDH$^+$)	1203.5	1191.7	
E(*t*Bu$_4$CBD) – E(*t*Bu$_4$CBDH$^+$)	1210.3	1190.5	

[a] Since the energy of H$^+$ is null, we have not included it in the relative energies.

6.8 kJ mol^{-1} more stable than tBu$_4$CBD at the B3LYP/6-31G(d) level. This is in contrast to earlier force-field[21] and semiempirical (MNDO)[22] calculations as well as to experimental findings (see previous discussion).[5] When the calculations are carried out at the B3LYP/6-311 + G(d,p)//6-31G(d) level, these values become 105.3 and -1.2 kJ mol^{-1}, respectively. The latter value agrees fairly well with the experimental result (≈ -10 kJ mol^{-1}).

The use of QCISD(T)/6-31G(d)//B3LYP/6-31G(d) leads to a profile (Figure 1, values in parentheses) for the parent compound, which is similar to that of the B3LYP calculations, although the difference between CBD and THD is increased by up to 129.2 kJ mol^{-1}.

The enthalpies and Gibbs free energies at 298 K obtained from the B3LYP/6-31G(d) calculations are given in Table 2. From this data, we can estimate GB values for THD and tBu$_4$THD to be 1050.9 and 1134.7 kJ mol^{-1}, respectively. The calculated gas-phase basicity of tBu$_4$THD is higher than the experimentally determined GB of 1035 ± 10 kJ mol^{-1}. The corresponding values of the proton affinity for THD and tBu$_4$THD obtained at the same level of theory are 1080.2 and 1171.2 kJ mol^{-1}, respectively.

In order to assess the influence of the basis set on the computed GB and PA values, we have carried out single-point calculations at the 6-311 + G(d,p)//6-31G(d) level which gives GB values for THD and tBu$_4$THD of 1026.3 and 1122.9 kJ mol^{-1}, respectively. The calculated GB value for tBu$_4$THD decreased by $\approx$12 kJ mol^{-1} and is closer to the experimental value of 1035 ± 10 kJ mol^{-1}. The PA values for THD and tBu$_4$THD obtained at this level of theory are, 1055.7 and 1159.4 kJ mol^{-1}, respectively. The PA of THD is very close to the previously calculated value at the G2 level of 1053 kJ mol^{-1}.[16]

In conclusion, B3LYP calculations, at the level we have used, cannot yield absolute GB or PA values. A very large basis set, prohibitive for molecules of the size of tBu$_4$THD, should be used. Nevertheless, the theoretical results confirm that tBu$_4$THD is a superbase in the gas phase.

Mechanistic aspects and transition states: We have studied the very exothermic reaction between THD and NH$_4^+$ in detail. As can be derived from the B3LYP/6-31G(d) energies given in Table 1, the energies of the final products (CBDH$^+$ and NH$_3$) are 205.5 kJ mol^{-1} below the reactants. Unless there is a kinetic control, that is, a very high activation barrier, it is expected that the reaction occurs spontaneously.

The potential surface presents two stationary points, **A** and **B** (Figure 2). The analysis of the frequencies of the harmonic vibrations shows that **A** corresponds to a minimum (ion-induced dipole complex) and **B** to a transition state (TS1). The energy of the transition state is 3.8 kJ mol^{-1} above the minimum and 52.7 kJ mol^{-1} below the isolated reactants (THD and NH$_4^+$). This kinetic data, a negative potential barrier with respect to the isolated reactants and extremely small with respect to the ion-induced dipole complex, clearly shows that the protonation of THD by ammonium is a process which takes place spontaneously with concomitant isomerization to CBD.

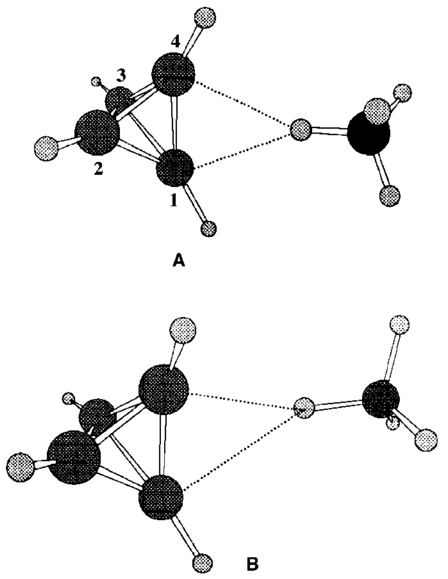

Figure 2. Geometries corresponding to B3LYP/6-31G(d) calculations of the two stationary points: the minimum THD···NH$_4^+$ (**A**) and the transition state TS (**B**).

When these energies were calculated at the QCISD(T)/6-31G(d) level, the values were strikingly similar: the exothermicity, -207.5 kJ mol^{-1} (see Table 1), the barrier with regard to the minimum 2.5 kJ mol^{-1}, and barrier with regard to the isolated reactants -48.1 kJ mol^{-1}. The small difference existing between the two stationary structures, at both levels of theory, indicates that the potential surface in this zone of the reaction path is very flat. Consequently, small energetic changes are associated with much larger geometric changes.

Table 2. Enthalpies and Gibbs free energies [Hartree; 1 Hartree = 2625.50 kJ mol^{-1}].

	B3LYP/6-31G(d)		B3LYP/6-311 + G(d,p)//B3LYP/6-31G(d)	
Minima	H_{298}[a]	G_{298}[b]	H_{298}[a]	G_{298}[b]
THD	– 154.573205	– 154.601960	– 154.617571	– 154.646326
CBD	– 154.610715	– 154.639448	– 154.656382	– 154.685115
CBDH$^+$	– 154.982285	– 155.012214	– 155.017305	– 155.047232
tBu$_4$THD	– 783.152453	– 783.231320	– 783.356233	– 783.435100
tBu$_4$CBD	– 783.147653	– 783.222528	– 783.354483	– 783.429358
tBu$_4$CBDH$^+$	– 783.596174	– 783.673517	– 783.795469	– 783.872811

[a] Enthalpy values were obtained from the absolute energies and the corresponding ZPE values and thermal corrections, evaluated at the B3LYP/6-31G(d) level. ZPE values were scaled by the empirical factor 0.9806.[23] [b] Gibbs free energy values were obtained from the enthalpy values and the corresponding entropy values, evaluated at the B3LYP/6-31G(d) level.

Table 3. Bond lengths [Å] and total energies [Hartrees; B3LYP/6-31G(d) results] of the species shown in Figure 2.

	C1–C4	C1–C2	C1–C3	C4–C2	C4–C3	C2–C3	C1–H	C4–H	H–N	Energy
THD	1.479	1.479	1.479	1.479	1.479	1.479	1.073	1.073	–	– 154.636663
Minimum **A**	1.516	1.477	1.477	1.477	1.477	1.470	2.148	2.148	1.069	– 211.552028
TS **B**	1.508	1.510	1.438	1.467	1.541	1.454	2.271	1.950	1.073	– 211.550625
CBDH$^+$	1.513	1.772[a]	1.388	1.513	2.200[a]	1.388	1.090	1.082	–	– 155.060871
CBD	1.578	2.067[a]	1.334	1.334	2.067[a]	1.578	1.084	1.084	–	– 154.675462

[a] Nonbonding distances

Geometrically,[24] the most important difference between the two stationary structures **A** and **B** is the relative position of the ammonium cation with respect to the THD molecule (Table 3). In the ion-induced dipole complex **A**, the distance between ammonium and THD is slightly greater than 2 Å ($d_{C-H} = 2.12-2.15$ Å), whilst in transition state **B**, the ammonium has already moved towards one of the THD carbons ($d_{C-H} = 1.95$ and 2.27 Å). Therefore, the reaction starts by an attack of the N^+–H towards one of the "edges" of THD, then the cation moves towards one of the corners of this edge (TS), and is followed by proton transfer. That the first step in protonation occurs on the edge was already known for tetrahedrane and other cage compounds, such as cubane and its derivatives.[17, 25]

The "reaction-path-following" method[26] showed that after the TS, the C4–C3 bond breaks first, then the proton transfer starts, and finally the second C–C bond (C1–C2) breaks.

Conclusions

Once *t*Bu$_4$THD is protonated, the resulting cation is very stable; the basicity of *t*Bu$_4$THD represents a record value. The experimental value for the gas-phase basicity of *t*Bu$_4$THD is close to the calculated GB of the parent molecule, THD. In the case of the model compound, THD, the profile of the reaction from THD$\cdots$NH$_4^+$ to CBDH$^+\cdots$NH$_3$ has been explored with ab initio calculations.

Experimental Section

Experimental determination of the gas-phase basicity of tetra-*tert*-butyltetrahedrane: An improved synthesis of tetra-*tert*-butyltetrahedrane (*t*Bu$_4$THD) has been described.[27] The experimental study of its gas-phase basicity was carried out by means of FT-ICR mass spectrometry[28] with a modified Bruker CMS47 mass spectrometer[29] used in previous studies.[30] A detailed description of the main features of this instrument is given in references [29, 30a]. The main modifications with respect to the standard instrument are given in reference [30a] The substantial field strength of its superconducting magnet, 4.7 T, allows the monitoring of ion–molecule reactions for relatively long periods of time, up to 120 s in some cases. A sufficiently long residence time of the ions in the cell is important whenever thermalizations of the ions is relevant, as in equilibrium studies.[28f] The ions are thermalized through collisions with the neutral species and radiation change with the surroundings.[31]

As in our previous studies,[30] the equilibrium constant, K_p, for the reaction given in Equation (2) was determined as follows: briefly stated, mixtures of $B_{ref}(g)$ and *t*Bu$_4$THD(g) of known partial pressures (total pressures in the range 5×10^{-7} to 5×10^{-6} mbar) were introduced to the high-vacuum section of the instrument, and were ionized by electron impact (nominal ionization energy of 11.5 eV). The corresponding protonated ions were generated by chemical ionization, the proton sources being the ionic fragments of B_{ref}. The fact that the constant ratio of the ion intensities corresponds to the attainment of equilibrium in Equation (2) was proven by means of double-resonance-like experiments.[30a] The pressure readings for the neutral reactants, as determined by the Bayard–Alpert gauge of the FT-ICR spectrometer, were corrected by means of the gauge sensitivity for each reactant. The gauge sensitivities relative (S_r) to N_2 have been estimated according to Bartmess and Georgiadis[32] by means of the average molecular polarizabilities, α(ahc), calculated according to Miller.[33]

Computational details: All energies were calculated with "density functional theory" (DFT) Becke3-LYP method[34] together with the standard basis sets 6-31G(d)[35] and 6-311 + G(d,p),[36] as implemented in the Gaussian 98 program.[37] All the reported structures are stationary points (minima or transition states) on the B3LYP/6-31G* potential energy surface. To check the B3LYP/6-31G (d) values, single point energy calculations of the most simple systems (THD, CBD, CBDH$^+$, NH$_3$ and NH$_4^+$) were carried out at the QCISD(T) level with the same set of base functions.[38]

Acknowledgements

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[1] The following abbreviations are used in this work: THD, tetrahedrane; THDH$^+$, protonated tetrahedrane; CBD, cyclobutadiene; CBDH$^+$, protonated cyclobutadiene; *t*Bu$_4$THD, tetra-*tert*-butyltetrahedrane; *t*Bu$_4$THDH$^+$, protonated tetra-*tert*-butyl-tetrahedrane; *t*Bu$_4$CBD, tetra-*tert*-butylcyclobutadiene; *t*Bu$_4$CBDH$^+$, protonated tetra-*tert*-butylcyclobutadiene.

[2] Summaries: a) G. Maier, *Angew. Chem.* **1974**, *86*, 491–505; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 425–438; b) A. Greenberg, J. F. Liebman, *Strained Organic Molecules*, Academic Press, New York, 1978; c) N. S. Zefirov, A. S. Koz'min, A. V. Abramenkov, *Russ. Chem. Rev. (Engl.)* **1978**, *47*, 163–171 d) G. Maier, *Angew. Chem.* **1988**, *100*, 317–341; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 309–332; e) V. I. Minkin, M. N. Glukhovtsev, B. Ya. Simkin, *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*, Wiley, New York, **1994**, p. 281.

[3] G. Maier, S. Pfriem, U. Schäfer, R. Matusch, *Angew. Chem.* **1978**, *90*, 552–553; *Angew. Chem. Int. Ed. Engl.* **1978**, *90*, 520–521.

[4] G. Maier, S. Pfriem, U. Schäfer, K.-D. Malsch, R. Matusch, *Chem. Ber.* **1981**, *114*, 3965–3987.

[5] G. Maier, S. Pfriem, K.-D. Malsch, H.-O. Kalinowski, K. Dehnicke, *Chem. Ber.* **1981**, *114*, 3988–3996.

[6] K. B. Wiberg, R. F. W. Bader, C. D. H. Lau, *J. Am. Chem. Soc.* **1987**, *109*, 985–1001

[7] H. Kollmar, *J. Am. Chem. Soc.* **1980**, *102*, 2617–2621.

[8] B. A. Hess, L. J. Schaad, *J. Am. Chem. Soc.* **1985**, *107*, 865–866.

[9] Besides *t*Bu$_4$THD and two of its isotopomers,[2d] seven additional isolable tetrahedranes have been synthesized,[10] in which one *tert*-butyl of *t*Bu$_4$THD is replaced by the following substituents: SiMe$_3$,[11] SiMe$_2$Ph,[12] SiMe$_2$OCHMe$_2$,[12] SiHMe$_2$,[12] GeMe$_3$,[13] CHMe$_2$,[14] adamantyl.[15]

[10] Summary: G. Maier, R. Wolf, F. Fleischer, GIT *Fachz. Lab.* **1992**, 506–511.

[11] a) G. Maier, D. Born, *Angew. Chem.* **1989**, *101*, 1085–1087; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1050–1052; b) G. Maier, D. Born, I. Bauer, R. Wolf, R. Boese, D. Cremer, *Chem. Ber.* **1994**, *127*, 173–189.

[12] a) G. Maier, R. Wolf, H.-O. Kalinowski, *Angew. Chem.* **1992**, *104*, 764–766; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 738–740; b) G. Maier, R. Wolf, H.-O. Kalinowski, R. Boese, *Chem. Ber.* **1994**, *127*, 191–200.

[13] G. Maier, R. Wolf, H.-O. Kalinowski, *Chem. Ber.* **1994**, *127*, 201–207.

[14] G. Maier, F. Fleischer, H.-O. Kalinowski, *Liebigs Ann.* **1995**, 173–186.

[15] G. Maier, H. Rang, D. Born, *Cage Hydrocarbons*, Wiley, New York, **1990**, 219–259.

[16] R. Notario, J. Elguero, *J. Chem. Soc. Chem. Commun.* **1995**, 1543–1544.

[17] I. Alkorta, J. Elguero, *Tetrahedron* **1997**, *53*, 9741–9748.

[18] G. Maier, R. Emrich, K.-D. Malsch, K.-A. Schneider, M. Nixdorf, A. Irngartinger, *Chem. Ber.* **1985**, *118*, 2798–2810.

[19] Experimental gas-phase basicities for the reference bases were taken from: E. P. L. Hunter, S. G. Lias, *J. Phys. Chem. Ref. Data* **1998**, *27*, 413–656.

[20] a) M. Decouzon, J.-F. Gal, P.-C. Maria, E. D. Raczynska, *Rapid Commun. Mass Spectrom.* **1993**, *7*, 599–602; b) E. D. Raczynska, P.-C. Maria, J.-F. Gal, M. Decouzon, *J. Phys. Org. Chem.* **1994**, *7*, 725–733.

[21] K. Mislow, W. D. Hounshell, personal communication; ref. [24] in W. T. Borden, E. R. Davidson, *Acc. Chem. Res.* **1981**, *14*, 69–76.

[22] A. Schweig, W. Thiel, *J. Am. Chem. Soc.* **1979**, *101*, 4742–4743.

[23] A. P. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502–16513.

[24] The calculated geometry of $t\mathrm{Bu}_4\mathrm{CBDH}^+$ compares very well with the experimental geometry of $t\mathrm{Bu}_4\mathrm{CBDH}^+$ (Scheme 1): C1–C4 1.524 vs 1.524 Å, C1–C2 1.826 vs 1.806 Å, C1–C3 1.413 vs 1.408 Å.

[25] I. Rozas, I. Alkorta, J. Elguero, *J. Phys. Chem. A* **1997**, *101*, 9457–9463; I. Alkorta, I. Rozas, J. Elguero, *Chem. Soc. Rev.* **1998**, *27*, 163–170.

[26] a) K. Fukui, *Acc. Chem. Res.*, **1981**, *14*, 363–368; b) C. González, H. B. Schlegel, *J. Chem. Phys.*, **1989**, *90*, 2154–2161; c) C. González, B. H. Schlegel, *J. Phys. Chem.*, **1990**, *94*, 5523–5527.

[27] a) G. Maier, F. Fleischer, *Tetrahedron Lett.* **1991**, 57–60; b) G. Maier, F. Fleischer, *Liebigs Ann.* **1995**, 169–172.

[28] a) *Gas-Phase Ion Chemistry, Vols. 1–3* (Ed.: M. T. Bowers), Academic Press, New York, **1979** (*Vols. 1 and 2*), **1984** (*Vol. 3*); b) "Fourier Transform Mass Spectrometry. Evolution, Innovation and Applications" *ACS Symp. Ser.* **1987**, *359*, 1–125; c) A. G. Marshall, F. R. Verdun, *Fourier Transforms in NMR, Optical and Mass Spectrometry*, Elsevier, Amsterdam, **1990**; d) *FT-ICR/MS: Analytical Applications of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry* (Ed.: B. Asamoto), VCH, Weinheim, **1991**; e) A. G. Marshall, C. L. Hendrickson, G. S. Jackson, *Mass Spectrom. Rev.* **1998**, *17*, 1–35; f) "Energetics of Stable Molecules and Reactive Intermediates", J.-L. M. Abboud, R. Notario, *NATO ASI Ser. Ser. C* **1999**, *35*, 281–302.

[29] F. H. Laukien, M. Allemann, P. Bischofberger, P. Grossmann, H. P. Kellerhals, P. Kofel, *ACS Symp. Ser.* **1987**, *359* 81–99.

[30] a) J.-L. M. Abboud, M. Herreros, R. Notario, M. Essefar, O. Mó, M. Yáñez, *J. Am. Chem. Soc.* **1996**, *118*, 1126–1130; b) J.-L. M. Abboud, M. Herreros, R. Notario, O. Mó, M. Yáñez, M. Regitz, J. Elguero, *J. Org. Chem.* **1996**, *61*, 7813–7818; c) J.-L. M. Abboud, O. Castaño, J. Elguero, N. Jagerovic, R. Notario, K. Sak, *Int. J. Mass Spectrom. Ion Proc.* **1998**, *175*, 35–40.

[31] M. Sena, J. M. Riveros, *J. Phys. Chem. A* **1997**, *101*, 4348–4391.

[32] J. E. Bartmess, R. M. Georgiadis, *Vacuum* **1983**, *33*, 149–153.

[33] K. J. Miller, *J. Am. Chem. Soc.* **1990**, *112*, 8533–8542.

[34] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; c) C. Lee, W. Yang. R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; d) P. J. Stephens, F, J, Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.

[35] a) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257–2261. b) M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265–3269.

[36] a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654; b) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comp. Chem.* **1983**, *4*, 294–301.

[37] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andrés, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian98*, Gaussian, Pittsburgh PA, **1998**.

[38] J. A. Pople, M. Head-Gordon, K. Raghavachari, *J. Chem. Phys.* **1987**, *87*, 5968–5975.

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